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14. ABSTRACT Among the least understood and least exploited aspects of nanoscience is dynamic coupling between directional translation at mesoscales (above ~50 nm) and changes in local chemical bonding (below ~1 nm). Such coupling underlies catastrophic failure of materials, operation of actuating polymers, behavior of polymer flows and chemical mechanosensing. Chemomechanics is an integration of the two conventional dynamic models into a single internally consistent, scale-independent framework that is essential for quantitative understanding and efficient exploitation of dynamic coupling across the "formidable gap" at ~1-50 nm. With AFOSR funding we have developed chemomechanics to guide molecular design of monomers for self-assessing and photoactuating polymers and to address such fundamental questions as the thermodynamic efficiency of direct light-to-motion energy conversion and the distribution of strains in polymer flows. Specifically, we have: 1. developed a predictive model of chemical kinetics that incorporates mechanical force as an explicit control parameter					
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FA9550-08-1-0072 *New method to acquire chemomechanical parameters of diverse chemical reactions.* PI: Roman Boulatov; PO: Charles Lee; Site: University of Illinois, Urbana, IL 61801

Final report.

The focus of our AFOSR-supported research has been to develop the theoretical and experimental methods the following question: How does the kinetic (or thermodynamic) stability of a localized reactive site in a long inert polymer changes as the polymer is stretched. This question has preoccupied polymer scientists since at least 1940 and the lack of models to answer it for an arbitrary reactive site, i.e., to predict changes in kinetic or thermodynamic stability of various monomers, is emerging as the major roadblock to efficient design of stress-responsive and actuating polymers, the dynamics of viscoelastic flows of polymers and the design of new (smart) delivery and storage materials.

Our major accomplishments during the reporting period have been:

1. to derive a statistical-mechanics expression of the rate constant of a single-barrier reaction in a stretched polymer as a function of the "mechanical" force stretching the polymer (chemomechanical kinetics). For Boltzmann-distributed constrained (mechanical) degree of freedom, a simple closed-form expression is obtained by approximating the free energy of the strain-free reactant and transition state as 2nd-order Taylor expansions. For other distributions, net rate constants are available by numeric integration of the master equation. In the simplest case of long flexible polymer, the mechanical coordinate is defined by the pair of atoms of the polymer whose separation is constrained.

2. to formulate and validate quantum-mechanically the local approximation of chemomechanical kinetics, i.e., the postulate that a single internal coordinate (i.e., internuclear distance) of the reactive site exist whose restoring force in the ground state and elongation (contraction) during the reaction equal the mechanical force and elongation (contraction) of the constrained (mechanical) coordinate. In other words, the mechanical degree of freedom of the polymer in the master equation can be replaced by a local molecular coordinate. The nature of the local coordinate is determined solely by the structure of the reactive site and the reaction mechanism and is independent of the length or the chemical composition of the rest polymer. Consequently, the local approximation allows, for the first time since the problem was posed by Eyring in 1940, to predict with useful accuracy, the rate of a local reaction in a polymer as it's being stretched, using only the readily available structural and kinetic properties of isolated reactive site (i.e., minimal reactant) without any empirical parameters.

3. to develop a simple, general experimental methodology to measure the kinetic stability of diverse monomers subject to a wide range of tensile forces and to apply it to diverse mechanistic classes of chemical reactions. For example, based on the local approximation and our experiments, we developed a simple intuitive model to estimate kinetic susceptibility of electrophilic sites in polymers to nucleophilic attack (e.g., by water), which is thought to be a major initiation mechanism of strain-induced polymer failure under many operating conditions (e.g., steam, highly ionic aqueous solutions). This model requires no quantum-mechanical calculations and allowed us to design monomers whose stability to nucleophilically-assisted degradation increases as the polymer is stressed. We have also discovered that certain monomers become more resistant to degradation under tensile strain, while most conventional polymers (e.g., polyamides, polyesters, polyethylene) fragment faster the more they are stretched. For example, our work suggests that overstretching a polymer in the presence of nucleophiles accelerates solvolysis of backbone C-O bonds but *inhibits* solvolysis of backbone Si-O bonds and has no effect on the susceptibility of the S-S bonds to reductive scission. Nucleophilic scission of backbone P-O bonds of phosphates and pyrophosphates is inhibited by overstretching a polymer, but dissociation of their side-chain P-O bonds is accelerated even though they are orthogonal to the straining axis. The diverse response is controlled by the difference, between the ground and transition states of the localized reaction, in the separation of two atoms that connect the electrophilic atom (C, Si,

P or S) to the rest of the polymer, regardless of the size or composition of the rest of the reactant. This intuitive model yields usefully accurate semi-quantitative predictions of the strain-induced changes in localized reactivity without quantum chemical calculations.

4. to develop a theoretically sound general molecular model of photomechanical energy conversion in photoresponsive polymers capable of guiding the design of new chromophores for practical propulsion strategies at nanoscale. Direct conversion of light into directional translation at the mesoscale is of intense contemporary interest. Photochemical actuation, in which propulsion results from concerted nuclear motion during local photochemical reactions offers unique attributes, e.g., potentially fast actuation cycles, high chemical and mechanical stability, flexible device design and operability at sub- μm scales and in ultra-thin films. Photoactuating materials contain chromophores (e.g., azobenzene) that have two isomers of significantly different molecular geometry dispersed in, or bound to, a polymer matrix with long-range order. Irradiation of the material enriched in one isomer results in bulk internal strain redistribution and hence directional mesoscale translation, if initially-dominant isomer is preferentially photoisomerized. Considerable effort has been devoted to maximizing photoinduced changes in the macroscopic aspect ratios of photoactuating materials by optimizing their mesoscopic structure (e.g., liquid-crystal elastomers).

Ultimately the performance of a photoactuating material is limited by the kinetics and thermodynamics of photochemical and thermal reactions of individual chromophores. Because these reactions occur in highly anisotropic environment under macroscopic constraints, little is known about how they affect the photomechanical behavior of the material. My group has developed a model for reversible and pseudoreversible isothermal photoactuation based on the Carnot-type formalism and used it to estimate the maximum single-chain power output, conversion efficiency and stall force of oligo stiff stilbene and azobenzene using experimentally measured parameters. Our goal for the next 3 years is to validate these calculations in individual macromolecules, understand empirically how the behavior of isolated macromolecules determines macroscopic actuation, develop a suite of new chromophores specifically optimized for operation against external loads of 10s of MPa and test them in materials.

5. to design a suite of mechanochromes for colorimetric and fluorimetric measurements of force distribution in stretched polymers. The behavior of long flexible polymers in liquid and solid flows has been intensely studied over the past 30 years. Yet, experimental methods to understand molecular details of the behavior remain very limited. We have developed latent chromophores or fluorophores that become absorbing/emissive when the polymer fragment they are part of is stretched above a well defined threshold force or strain (mechanochromes) that would allow us to measure distributions of restoring forces of macromolecules (or their fragments) with sub- μm resolution first in laminar dilute solutions and later in complex systems, such as top layers of bulletproof vests and aircraft coatings under realistic operating conditions. We are working on strategies to increase the spatial resolution of strain/force distribution mapping within strained materials using active chemistry.

6. to outline molecular design criteria for practical photothermal energy storage in form of strained chromophores. Storing energy of sunlight as high-energy chemical bonds offers complementary capabilities to photovoltaics and solar heat concentrators. Such "solar heat batteries" were long deemed impractical because of their perceived explosion hazard (chemists have long thought - incorrectly - that increasing the energy content of a reaction inevitably increases its rate). Building on our findings of simple reactions that show the inverted relationship between standard and activation free energies we designed computationally stiff-stilbene and isoindigo derivatives that could store up to 50% (33 kcal/mol) of absorbed photon energy as strain energy. In the future, we will validate the estimates experimentally, lower the wavelength that generates the strained state, synthesize the polymers and test them in low-temperature heat engine.